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Calculated Lattice Specific Heats for Seven bcc Elements*

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A brief review is given of the method by which the author has obtained frequency spectra for a Born–von Kármán central force model for bcc elements, and of the method in which these spectra are utilized to calculate specific heats. Specific heats have been calculated for the elements lithium, sodium, potassium, iron, tungsten, vanadium, and molybdenum, from the measured elastic constants reported by others. The corresponding Debye characteristic temperature Θ as a function of absolute temperature is shown on a graph for each element along with the experimental low-temperature values obtained by others. An upper limit to the temperature range for which de Launay's method for finding $\Theta(T)$ is valid, is given for each element.

INTRODUCTION

THE author has previously reported[1,2] the results of a program for determining the frequency spectra for lattice vibrations in bcc elements, and has described[3] a method for the calculation of lattice specific heats from these spectra. The next section contains a brief review of these programs.

The results of the calculation of the specific heats for the elements lithium, sodium, potassium, iron, tungsten, vanadium, and molybdenum are presented in terms of the Debye characteristic temperature Θ as a function of absolute temperature. For each element (except vanadium), a graph is given which shows the calculated Θ and that determined from experimental measurements, in the region of low absolute temperature. The results of the present calculations are compared to those obtained by de Launay's method, for the low-temperature region.

The final section contains a discussion of the results.

BACKGROUND

The spectra in I were determined for the simple Born–von Kármán model with only central interactions between nearest and next-nearest neighbors. The secular equation was solved for 42 925 values of the propagation vector for plane-wave solutions to the equations of motion for a representative atom. The three solutions for each vector were classified according to magnitude, and the frequency spectrum was obtained. Spectra in the form of tabular histograms are given in I for 18 values of the ratio β of the next-nearest neighbor force constant to that for nearest neighbors. The value of β for a bcc element may be determined from its measured elastic constants c_{11}, c_{12}, and c_{44} by the relation $\beta=(c_{11}-c_{12})/3c_{44}$. Elastic constant values have been reported for the bcc elements lithium, sodium, potassium, iron, tungsten, molybdenum, and vanadium. Table I lists the value of β calculated from these elastic constants and the lowest absolute temperature at which the constants were measured.

In II it is explained that the choice of vectors for which the secular equation was solved, caused the frequency spectra to be inaccurate at low frequencies. In turn, the values of specific heats at low temperatures calculated from the spectra were wrong, since these low frequencies are responsible for the major contribution to the specific heat values at low temperatures. In addition, it was found necessary at low temperatures to use an increment in frequency, considerably smaller than that on which the tabular histograms in I were based. A new histogram for smaller frequency intervals was constructed over a portion of the low-frequency range from the expression

$$f(x)=c_1x^2+c_2x^4. \tag{1}$$

The constants c_1 and c_2 and the exact frequency range for each of the 8 β values are given in II. The form of f in Eq. (1) was suggested by the work of de Launay,[4]

TABLE I. Values of β from measured elastic constants.

Element	β	T(°K)[a]
Li[b]	0.072	78
Na[c]	0.0897	90
K[c]	0.11	77
Fe[d]	0.28	298
W[e]	0.67	300
V[f]	0.82	4.2
Mo[g]	0.86	300
Mo[h]	0.98	77

[a] Lowest temperature at which elastic constants were measured.
[b] H. C. Nash and C. S. Smith, J. Chem. Phys. Solids **9**, 113 (1959).
[c] See reference 4, p. 268, Table V. O. Bender, Ann. Physik **34**, 359 (1939).
[d] W. B. Daniels, unpublished (1958), communicated to the author by C. S. Smith; B. S. Chandrasekhar and J. A. Rayne, Bull. Am. Phys. Soc. **6**, 76 (1961), have reported values extrapolated to 0°K, from which the value of β is approximately the same.
[e] See reference 4, p. 268, Table V; S. J. Wright, Proc. Roy. Soc. (London) **A126**, 613 (1930); J. de Klerk, and D. I. Bolef, Bull. Am. Phys. Soc. **6**, 76 (1961), have reported measurements at 77°K, from which the value of β is approximately the same.
[f] G. A. Alers, Phys. Rev. **119**, 1532 (1960).
[g] See reference 4, p. 268, Table V. M. J. Druyvestan, Physica **8**, 439 (1941).
[h] J. de Klerk and D. I. Bolef, Bull. Am. Phys. Soc. **6**, 76 (1961).

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[1] C. B. Clark, Bull. Am. Phys. Soc. **5**, 41 (1960).

[2] C. B. Clark, J. Grad. Research Center **24**, 10 (1961), cited as I, hereafter.

[3] C. B. Clark, to be published in a forthcoming issue of J. Grad. Research Center; cited as II, hereafter.

[4] J. de Launay, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 219.

in connection with the development of his method for calculating the Debye characteristic temperature Θ as a function of absolute temperature at low temperatures [see Eq. (8.18) of the reference cited]. The variable x is related to the circular frequency ω by

$$x=\omega\{(4ac_{44}/M)[2+(3\beta/2)]\}^{-\frac{1}{2}}, \tag{2}$$

where a is the lattice cube edge length and M is the mass of one atom. The variable x ranges from zero to unity as ω ranges from zero to the maximum normal mode frequency.

The expression for the specific heat C_V (per gram-atomic weight) is given by

$$C_V/3R=\frac{H}{N}\sum_{i=1}^{200}\frac{(Ax_i/T)^2(c_1x_i^2+c_2x_i^4)}{\sinh^2(Ax_i/T)} +\frac{1}{N}\sum_{j=n+1}^{100}\frac{(Ax_j/T)^2f_j}{\sinh^2(Ax_j/T)}. \tag{3}$$

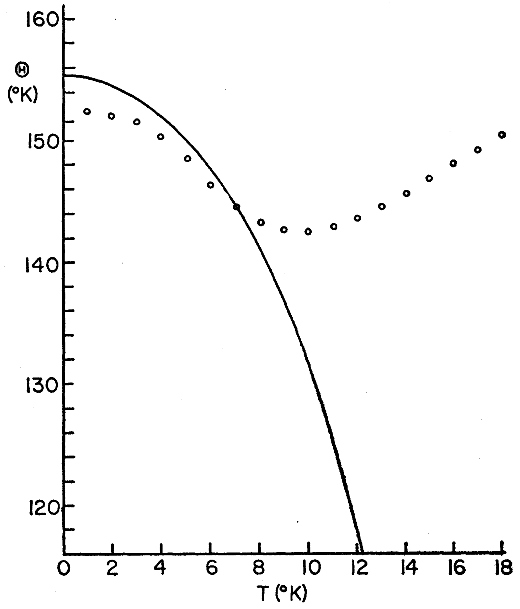

FIG. 1. $\Theta(T)$ for sodium. The curve was obtained by de Launay's method; the circles represent calculations based on Eq. (3) in the text.

The range in x over which the new histogram is constructed is from zero to $n\times10^{-2}$, where the values of n are given in II. H is a normalization factor which insures that the area under the new histogram is the same as that under the corresponding portion of the old histogram. The other quantities in Eq. (3) are given by $A=(\hbar/k)[(ac_{44}/M)[2+(3\beta/2)]]^{\frac{1}{2}}$; where $\hbar$ is Planck's constant divided by 2π and k is Boltzmann's constant, $x_i=(i-\frac{1}{2})(\frac{1}{2}n\times10^{-4})$, $x_j=(j-\frac{1}{2})\times10^{-2}$, the f_j are the histogram values, $N=\sum_{j=1}^{100}f_j$, and R is the universal gas constant.

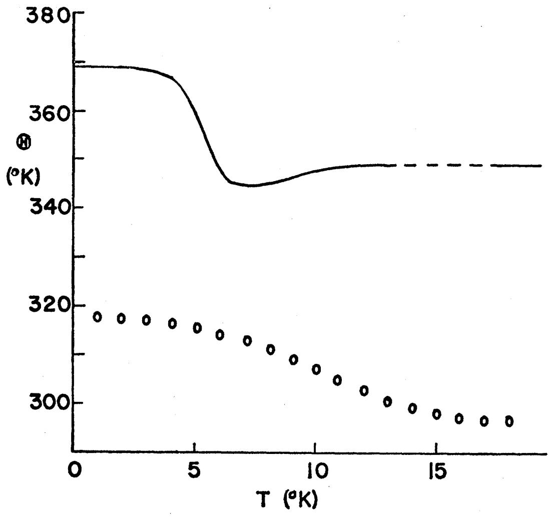

FIG. 2. Comparison of experimental and theoretical $\Theta(T)$ for lithium. The curve represents results reported by Roberts; the circles represent calculations based on Eq. (3) in the text.

RESULTS OF THE CALCULATIONS

The Remington Rand Univac Scientific 1103 electronic computer at S. M. U. was programmed to calculate the values of $C_V/3R$ from Eq. (3) for the seven bcc elements listed in Table I. The histograms for the first seven values of β are given in I. The histogram for $\beta=0.98$ was obtained by linear interpolation between the $\beta=0.9$ and $\beta=1.0$ histograms.

The calculations were made for temperatures at intervals of 1° from 1°K to 20°K, at intervals of 2° from 20°K to 40°K, at intervals of 5° from 40°K to 100°K, and at intervals of 10° from 100°K to 600°K (a total of 92 different temperatures). The wide range insured that $C_V/3R$ would approach the "Dulong and Petit value" of unity, even though for some of the substances this includes temperatures greater than the melting temperature. For all of these substances, n was set equal to zero for $T\geqq40$°K, so that only the second summation in Eq. (3) was used.

For comparison of specific heat values it is conventional, and desirable, to employ the Debye Θ as a function of temperature. Essentially, one equates the

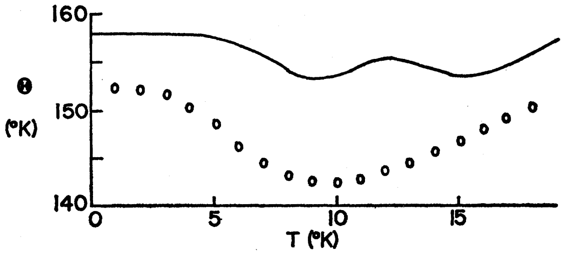

FIG. 3. Comparison of experimental and theoretical $\Theta(T)$ for sodium. The curve represents experimental results reported by Roberts; the circles represent calculations based on Eq. (3) in the text.

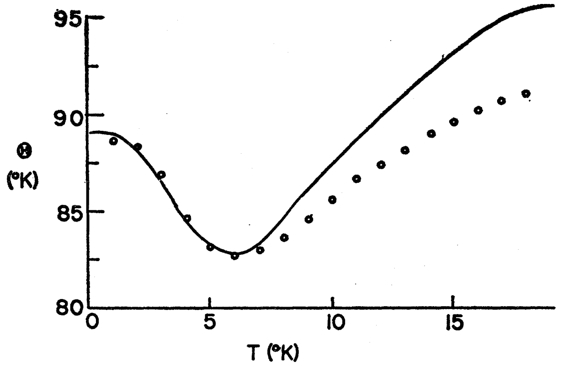

Fig. 4. Comparison of experimental and theoretical $\Theta(T)$ for potassium. The curve represents experimental results reported by Roberts; the circles represent calculations based on Eq. (3) in the text.

value of C_V at a certain temperature to Debye's expression and solves for Θ, thus obtaining a value of Θ for each T. This process is facilitated by the use of Beattie's table.[5] In a separate program for the Univac, the Beattie table was read into the machine from standard 80 column cards. (Arrangements may be made with the S. M. U. Computing Laboratory to obtain duplicates of these cards which may be used for data input on most electronic computers.) A linear interpolation routine was used to find the value of Θ corresponding to each value of $C_V/3R$.

Many methods have been proposed for computing Θ at low temperatures from elastic constants.[6] The method proposed by de Launay[4,7] is easily applied for the model for which the histograms were calculated. The values of the parameters f and f' for this method were determined by graphical interpolation, except that the values of f' for tungsten, vanadium and molybdenum were obtained by extrapolation. The parameter s used by de Launay is $3\beta/2$ for bcc elements. Figure 1 shows a plot of the $\Theta(T)$ found from de Launay's method for sodium and the points calculated from Eq. (3). This result is typical of those obtained for all seven substances. The differences in Θ at absolute zero amounted to about 3% or less, with the values calculated from de Launay's method always the greater. More information from the study of such comparisions will be given in the next section of this paper.

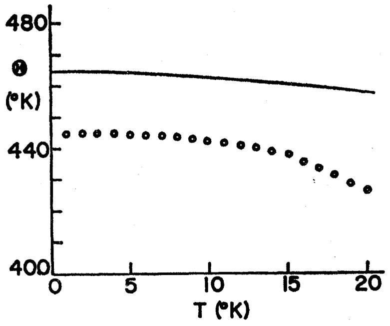

Fig. 5. Comparison of experimental and theoretical $\Theta(T)$ for iron. The curve represents experimental results reported by Keesom and Kurrelmeyer; the points calculated from their data were widely scattered about the curve. The circles represent calculations based on Eq. (3) in the text.

The simple model used here will, no doubt, prove to be an inadequate representation of the bcc elements. However, in the author's opinion, it is essential to know what results from this simple model in order to understand better the physical significance of the more complicated models, which may yield better results in terms of agreement with experiment. One would, in general, hope for agreement between experiment and a theory using harmonic wave solutions, only in the low temperature region. For this reason, the comparisons with experimental data are restricted to the low-temperature region.

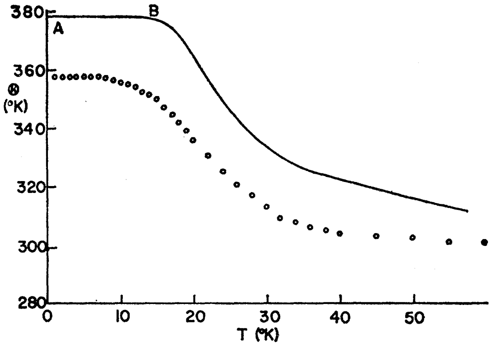

Fig. 6. Comparison of experimental and theoretical $\Theta(T)$ for tungsten. The curve was obtained by Parkinson from experimental results reported by Waite, Craig, and Wallace, by Zwikker, and by Lange; the circles represent calculations based on Eq. (3) in the text.

Lithium. Figure 2 shows the experimentally determined $\Theta(T)$ curve for lithium which has been reported by Roberts,[8] together with the first 18 values obtained by the author from Eq. (3).

Sodium. Figure 3 shows the experimentally determined $\Theta(T)$ curve for sodium which has been reported by Roberts.[8] The circles represent the first 18 values obtained by the author from Eq. (3).

Potassium. Figure 4 shows the experimentally determined $\Theta(T)$ curve for potassium which has been reported by Roberts.[8] The circles represent the first 18 values obtained by the author from Eq. (3).

Iron. Figure 5 shows the experimentally determined $\Theta(T)$ curve for iron. The data were reported by Keesom and Kurrelmeyer.[9] Their values of C_V were used with

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[5] J. A. Beattie, J. Math. Phys. **6**, 1 (1926–27).

[6] G. A. Alers and J. A. Neighbours, Revs. Modern Phys. **31**, 675 (1959).

[7] J. de Launay, J. Chem. Phys. **22**, 1676 (1954); **24**, 1071 (1956); **30**, 91 (1959).

[8] L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 744 (1957).

[9] W. H. Keesom and B. Kurrelmeyer, Physica **6**, 633 (1939).

TABLE II. The upper bound T_u for de Launay's method.

Element	Θ_0(°K) (de Launay's Method)	$S=3\beta/2$	T_u(°K)
Li	323	0.11	15
Na	155	0.13	7
K	92	0.16	5
Fe	458	0.42	31
W	369	1.0	24
V	395	1.2	31
Mo	456	1.3	36
Mo	474	1.5	37

the Univac program which employs the Beattie Table and the values of Θ were found from which the curve was obtained. The points were widely scattered about the curve. The circles represent the first 20 values found by the author from Eq. (3).

Tungsten. Figure 6 shows an experimentally determined $\Theta(T)$ curve, as it appears in a review article by Parkinson.[10] The data up to 15°K were obtained by Waite, Craig, and Wallace.[11] The data at higher temperatures were obtained by Zwikker[12] and by Lange.[13] The circles represent the first 34 values obtained by the author from Eq. (3).

Vanadium. No figure is shown for vanadium. Some C_V data have been obtained by Corak *et al.*[14] Data for the normal state were obtained below 6°K by the use of high magnetic fields to prevent the transition to the superconducting state. The electron contribution to the measured specific heat is very large at these temperatures. When the electron term is subtracted from the measured value of C_V, the remainder which is designated as the lattice contribution, contains all of the experimental error, which is too large to allow a determination of deviations from the Debye T^3 form.[15] For a comparison of the type made for the other 6 elements, one would need empirical results obtained with much greater accuracy and over a wider temperature range than characterized the work cited in footnote 14. It should be noted that this is not an adverse criticism of that effort, since it was motivated by an entirely different purpose than that which this author has in mind.

Molybdenum. Figure 7 shows the experimentally determined $\Theta(T)$ curve which was reported by Horowitz and Daunt.[16] Between the time calculations for the histograms in I and those from Eq. (3) were made, new elastic constant measurements for Mo were reported, which yielded a quite different value of β. The solid circles represent values obtained by the author from Eq. (3), with the older values of elastic constants, while the open circles are based on the newer elastic constants.

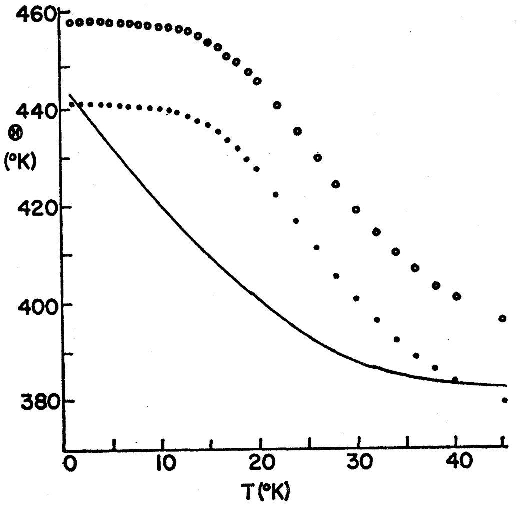

FIG. 7. Comparison of experimental and theoretical $\Theta(T)$ for molybdenum. The curve represents experimental results reported by Horowitz and Daunt; the solid and open circles represent calculations from Eq. (3) in the text with two different sets of elastic constants—solid, older values, open, newer values.

DISCUSSION OF RESULTS

The values of Θ at low temperatures found from Eq. (3) show the same general form near absolute zero as those obtained by de Launay's method. For the elements characterized by values of β greater than 0.6, the $\Theta(T)$ curve from the present work is "flatter" at absolute zero than that from de Launay's method. The temperature T_u at the point of intersection of the two Θ curves represents an upper bound, although not the least upper bound, for the temperature range for which de Launay's method is valid. Table II lists the value of Θ_0 from de Launay's method, the value of the parameter $s=3\beta/2$, and that of T_u for the eight cases for which the author has made calculations.

The good agreement between the present theory and the experimental values for potassium (see Fig. 4) in the temperature range up to 7°K, is surprising. Each of the elements is metallic and it is rather well established that atoms of metals have important forces of interaction other than the two central forces included in the model on which the present work is based. The present results should aid one in understanding the contribution made by these additional forces as results are obtained for models which include them.

The $\Theta(T)$ values found from Eq. (3) all exhibited the same general form: zero slope at $T=0$; decrease in

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[10] D. H. Parkinson, *Reports on Progress in Physics* (The Physical Society, London, 1958), Vol. 21, p. 226.

[11] T. R. Waite, R. S. Craig, and W. E. Wallace, Phys. Rev. **104**, 1240 (1956).

[12] C. Zwikker, Z. Physik **52**, 668 (1928).

[13] F. Lange, Z. physik Chemie **110**, 343 (1924).

[14] W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **102**, 656 (1956).

[15] The discussion concerning the data from the work cited in footnote 14 is the author's interpretation of a private communication from C. B. Satterthwaite.

[16] M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953).

Θ with increasing T to a minimum which occurred at values of T ranging from 6°K for potassium to over 100°K for Mo; the increase in Θ with increasing T beyond the minimum tends to be more rapid for those substances having lower values of β; at T much greater than that for minimum Θ, the value of Θ becomes practically constant (little different from the minimum Θ for the substances having large β).

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Specific Heats of Dilute Au-Co Alloys between 1.2° and 5°K

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The specific heats of six specimens of dilute Au-Co alloys were measured between 1.2° and 5°K. Cobalt concentration of these samples lay between $\frac{1}{2}$ and $3\frac{1}{2}$ at.%. The specific heat is greater than that of pure gold at all alloy concentrations, with the excess at the higher temperatures being linear in temperature and proportional to the $\frac{3}{2}$ power of concentration for samples containing less than 2 at.% of cobalt. At the lower temperatures the specific heat excess is no longer linear in temperature, but diminishes less rapidly with decreasing temperature. The character of the specific heats of these Au-Co alloys is found to be very similar to the specific heats of dilute Cu-Co alloys.

INTRODUCTION

THESE measurements of the low-temperature specific heats of dilute gold-cobalt alloys constitute one of a series of investigations of the specific heats of dilute alloys of paramagnetic ions in noble metals.[1,2] It is expected that such data will be of value in providing the basis for a clearer insight into the mechanism of magnetic interactions in metals.

At present, quite complete resistance and magnetoresistance data exist for the entire set of dilute alloys of paramagnetic ions in noble metals.[3,4] Resistivities are found to have a maximum followed by a minimum, or just a minimum, as the temperature increases from absolute zero. In both cases, existence of the minima can be accounted for by the ferromagnetically coupled ion pair scattering proposed by Brailsford and Overhauser,[5] while the maxima seem to be associated with the reduction of spin-disorder scattering accompanying a large-scale magnetic ordering.

Susceptibility measurements,[3] on the other hand, are only available for a few members of this class of alloys, and are unreliable in some cases because of the high impurity content of the specimens used. However, recent susceptibility measurements using high purity materials do show obvious correlation with the resistivity data. Cu-Mn[6–9] and Ag-Mn[7,10] both possess resistivity maxima and are antiferromagnetically ordered at low temperatures with susceptibilities that are similar to each other in character. Cu-Co[11] exhibits only a resistivity minimum and yet has a negative Curie temperature as measured from the high-temperature data. However, its susceptibility increases very rapidly near absolute zero, indicating that a cooperative antiferromagnetic ordering is not taking place. Susceptibility measurements for Cu-Fe[12,13] have been made from 300°K down to liquid hydrogen temperatures and appear to be quite similar in character to measurements for Cu-Co, with no indication of long-range ordering above 14°K. And as might be expected, Cu-Fe exhibits only a resistivity minimum.[4]

Specific heat data are now available for dilute alloys of Cu-Mn,[1] Ag-Mn,[14] Cu-Co,[2] and Cu-Fe,[4] in addition to the present measurements on Au-Co. The data on

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[1] J. E. Zimmerman and F. E. Hoare, J. Phys. Chem. Solids **17**, 52 (1960).

[2] L. T. Crane and J. E. Zimmerman, Phys. Rev. **123**, 113 (1961).

[3] See A. N. Gerritsen, Physica **25**, 489 (1959) for a compilation of references concerning alloys of paramagnetic ions in noble metals.

[4] J. P. Franck, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).

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[11] I. S. Jacobs and R. W. Schmitt, Phys. Rev. **113**, 459 (1959).

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